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6. AUTHORS Todd Emrick, Al Crosby			5d. PROJECT NUMBER		
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14. ABSTRACT This project advanced the chemistry of functional nanoparticles and used these particles in advanced materials assembly for the fabrication of nanoparticle-based mesostructures. These hybrid materials possess extremely high inorganic weight fraction, yet benefit from the processibility offered by organic/polymer ligands, and the robustness resulting from ligand cross-linking post-assembly. The project developed a facile evaporative assembly method, termed flow coating, that affords nanoparticle-based ribbons that were studied for their fundamental features including 1) the shape and limitations of their dimensions, 2) their conductivity when employing metallic					
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Report Title

Final Report: Robust Nanoparticles

ABSTRACT

This project advanced the chemistry of functional nanoparticles and used these particles in advanced materials assembly for the fabrication of nanoparticle-based mesostructures. These hybrid materials possess extremely high inorganic weight fraction, yet benefit from the processability offered by organic/polymer ligands, and the robustness resulting from ligand cross-linking post-assembly. The project developed a facile evaporative assembly method, termed flow coating, that affords nanoparticle-based ribbons that were studied for their fundamental features including 1) the scope-and-limitations of their dimensions, 2) their conductivity when employing metallic nanoparticles in the assembly, and 3) their propensity to twist into helical structures irrespective of the nanoparticle (or polymer) composition used in the assembly. The ribbons identified in this project exhibited force-extension behavior described by a combination of elastic and surface energies. The macroscale mechanical properties of these ribbons, along with the inherent nanoscale properties of the particles, provide tunable multifunctionality and open numerous opportunities for applications in sensing, self-healing, and mechanical reinforcement applications.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/27/2013	1.00 Dong Yun Lee, Jonathan T. Pham, Jimmy Lawrence, Cheol Hee Lee, Cassandra Parkos, Todd Emrick, Alfred J. Crosby. Macroscopic Nanoparticle Ribbons and Fabrics, Advanced Materials, (03 2013): 0. doi: 10.1002/adma.201203719
12/28/2014	4.00 Jonathan T. Pham, Jimmy Lawrence, Gregory M. Grason, Todd Emrick, Alfred J. Crosby. Stretching of assembled nanoparticle helical springs, Physical Chemistry Chemical Physics, (03 2014): 10261. doi: 10.1039/c3cp55502j
12/28/2014	5.00 Jimmy Lawrence, Jonathan T. Pham, Dong Yun Lee, Yujie Liu, Alfred J. Crosby, Todd Emrick. Highly Conductive Ribbons Prepared by Stick–Slip Assembly of Organosoluble Gold Nanoparticles, ACS Nano, (02 2014): 0. doi: 10.1021/nn4057726
12/29/2014	2.00 Xiangji Chen, Jimmy Lawrence, Sangram Parekar, Todd Emrick. Novel Zwitterionic Copolymers with Dihydrolipoic Acid: Synthesis and Preparation of Nonfouling Nanorods, Macromolecules, (01 2013): 119. doi: 10.1021/ma301288m
12/29/2014	3.00 Jonathan T. Pham, Jimmy Lawrence, Dong Yun Lee, Gregory M. Grason, Todd Emrick, Alfred J. Crosby. Highly Stretchable Nanoparticle Helices Through Geometric Asymmetry and Surface Forces, Advanced Materials, (12 2013): 6703. doi: 10.1002/adma.201302817
TOTAL:	5

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

J.T. Pham, J. Lawrence, G. M. Grason, D.Y. Lee, T. Emrick, A.J. Crosby. "Nanoparticle assemblies: helical ribbons and flexible fabrics." New England Workshop on the Mechanics and Materials of Structures poster session, Brown University, Providence, RI. September 2012.

A.J. Crosby. "Hierarchical Materials Mechanics." MIT Department of Mechanical Engineering Seminar Series, Cambridge, MA. November 2012.

J.T. Pham, J. Lawrence, D.Y. Lee, G.M. Grason, T. Emrick, A.J. Crosby. "Geometry controlled formation of nanoparticle helical ribbons." American Physical Society, Baltimore, MD. March 2013.

A.J. Crosby. "Hierarchical Materials Mechanics." Army Research Laboratory, Aberdeen Proving Grounds, MD. March 2013.

T. Emrick. "Nanoscale Hybrid Materials Assembly." Aberdeen Proving Grounds, Aberdeen, MD. February 2013.

A.J. Crosby. "Draping Materials: Enabling Advanced Adhesives and Multifunctional Technologies." Plenary Lecture at Virginia Tech Technical Conference and Review, Blacksburg, VA, October 2013.

A.J. Crosby. "Draping Materials: Nanoparticle Ribbons." MIT Polymer Program Seminar Series, Cambridge, MA, December 2013.

A.J. Crosby. "Draping Materials: Enabling Advanced Adhesives and Multifunctional Technologies." Golden Gate Polymer Forum, Mountain View, CA, February 2014.

A.J. Crosby. "Draping Materials: Enabling Advanced Adhesives and Multifunctional Technologies." Mechanical Science & Engineering Department Seminar, University of Illinois Urbana-Champaign, February 2014.

A.J. Crosby. "Draping Materials: Enabling Advanced Adhesives and Multifunctional Technologies." Triangle MRSEC Seminar, Duke University, Durham, NC, February 2014.

A.J. Crosby. "Nanoparticle Ribbons and Grids." PPG, Pittsburgh, PA June 2014.

T.Emrick. "Responsive Nanoparticles and Polymers" Aberdeen Proving Grounds. July 24 2014.

T. Emrick "Responsive Nanostructures in Solution and at Interfaces". Spring 2014 American Chemical Society meeting. Dallas TX. March 2014.

Number of Presentations: 13.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Emrick - National Academy of Inventors
Emrick - Fellow, American Chemical Society

Emrick - Fellow, PMSE Division of the American Chemical Society
Emrick - Carl S. Marvel Creative Polymer Chemistry Award

Crosby - Northwestern Univ. Early Career Alumni Achievement in Materials Science
Crosby - College of Natural Sciences Outstanding Research Award
Crosby - ESPCI ParisTech – Michelin Visiting Professorship

Pham - Chateaubriand Fellowship

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>Discipline</u>
Jimmy Lawrence	0.90	
Jeffrey Dewey	0.05	
Cheol Hee Lee	0.05	
Jonathan Pham	0.08	
Yujie Liu	0.25	
Satyan Choudhary	0.17	
Minchao Zhang	0.08	
Shruti Rattan	0.17	
FTE Equivalent:	1.75	
Total Number:	8	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>National Academy Member</u>
Todd Emrick	0.10	
Al Crosby	0.10	
FTE Equivalent:	0.20	
Total Number:	2	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Jimmy Lawrence

Jonathan Pham

Total Number: 2

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Scientific Progress and Accomplishments.

I. Problem studied.

This ARO funded project enabled Emrick and Crosby to advance the chemistry and materials aspects of nanoparticle-based mesostructures, with these advances leading to novel nanoparticle-based architectures through evaporative deposition techniques. Over the course of the project, new ligands-functionalized nanoparticles were synthesized and tailored for the solution conditions needed for effective evaporative deposition. Evaluation of the mechanical properties of the resultant mesostructures confirmed the exceptionally robust nature of covalently interconnected nanoparticulate structures.

II. Most important results. The primary results of the project are summarized in five inter-related segments (A-E) below.

A. The preparation of macroscopic ribbons and fabrics from functional nanoparticles.

This portion of the project highlighted our ability to prepare fabric-like materials by “stitching” nanoparticles into hierarchical structures. Such structures comprised multiple length scales (from nanoscale thickness to microscale width to macroscale length), while maintaining the inherent desirable properties of the nanoparticles. For the example of CdSe quantum dots (QDs), unique evaporative deposition assembly processes were combined with functionalized nanoparticles to create ribbons were a single nanoparticle thick (measuring vertically from the substrate), as thin as 200 nm in width $x - y$ plane), and as long as 10 cm or more. These structural dimensions afford the ribbons with a great deal of flexibility. Through the combination of similarly sized polymer ligands connecting rigid NPs, a new balance of mechanical properties arises that mimic those of single polymer molecules but on a much larger scale. The ribbons proved virtually inextensible along their axis, controlled by the strength of covalent bonds, yet were seen to bend with ease due to the rotational freedom of their interparticle connectivity. Such combination of length scales in these nanoparticle-based ribbons is unprecedented, and opens new avenues for creating flexible conducting and semiconducting materials in a variety of simple or complex geometries.

B. Conducting nanoparticle-based ribbons: preparation and electronic characterization.

In this aspect of the project, flow-coating techniques for nanoparticle assembly into hierarchical structures was applied to Au NPs, intended to determine whether such structures would exhibit conductive properties inherent to the NPs. Au NP ribbons were thus prepared from surfactant-free organosoluble Au NPs, using flow-coating in a controlled, stick slip assembly that promoted NP deposition into densely packed, multilayered structures. Centimeter-scale long Au NP ribbons with precise periodic NP spacing were obtained in rapid fashion, up to 2 orders-of-magnitude faster than previously reported NP assembly methods. These Au NP ribbons exhibited linear ohmic response, with conductivity that varied with the composition of the ligand headgroup (thiol vs amine vs carboxylate). Controlling NP percolation during sintering (e.g., by adding a small weight percentage of polymer to retard rapid NP coalescence) enabled the formation of ribbons with high conductivity, on par with thermally sintered conductive adhesives.

C. Examination of stretching of nanoparticle-based springs.

This part of the project exploited the facile, evaporative assembly method, termed flow coating, to create NP-based ribbons that subsequently formed helical structures. We examined the stretching properties of these helical ribbons, which are nanometers thick, sub-micron in width, and arbitrarily long. The force-extension behavior was well-described by the elastic and surface energies, which were used as a guideline for their design. In addition, we showed that the mechanical properties may be tuned by changing the ribbon dimensions or material composition to yield a different stiffness. These macroscale mechanical properties, along with properties inherent to the nanometer length scale of the NPs, provide tunable multi-functionality.

D. Stretching nanoparticle-based helices.

In this work, we studied how surface forces dictate deformation and mechanics of soft materials or structures at small size scales. Specifically, the elastocapillary length, defined as the ratio of surface tension to elastic modulus, determines the size and conformation of macroscopic objects, including those with extreme flexibility. While a three-phase contact line can exert a capillary force, when the asymmetry of a capillary line is absent, shape transformations disappear and surface forces are no longer visible. We showed that the long, slender and flexible ribbons produced by flow coating of nanoparticle solutions, with asymmetric cross-sections and thickness on a similar order to the elastocapillary length, can amplify the inherent balance of interfacial tension and elasticity to reveal a new driving force for shape transformation into helices. This new mechanism revealed mechanically robust helices derived not only from NPs, but also from conventional polymers, thus offering a wide range of fundamentally new materials and potential applications.

E. Zwitterion-coated non-fouling nanorods.

This project led to the development of new polymer chemistry and the use of new polymers for functionalization of nanoparticles and nanorods. For example, we synthesized hydrophilic, zwitterionic copolymers containing pendent disulfide and dithiol groups along a phosphorylcholine methacrylate backbone. These novel copolymers were prepared by controlled free radical copolymerization of two monomers, specifically methacryloyloxyethyl phosphorylcholine (MPC) and the methacrylate of lipoic acid (LA), using reversible addition-fragmentation chain transfer (RAFT) polymerization. The polymers obtained were reduced from the

disulfide to the free thiol form, affording hydrophilic polymers with dihydrolipoic acid (DHLA) pendent groups. Poly(MPC-co-DHLA) proved useful for surface functionalization of gold nanorods (Au NRs), resulting in removal of the cationic surfactant stabilizing layer present initially on the Au NRs. Au NRs coated with poly(MPC-co-DHLA) proved stable against challenging conditions, and resisted cyanide ion digestion. Au NRs coated with poly(MPC-co-DHLA) also showed nonfouling properties resulting from their surface coating, and the noncytotoxicity of these structures was confirmed in the presence of live cells. The novel polymer materials and the methodology we describe hold promise for enabling new opportunities that utilize surface coated metallic and semiconductor nanostructures in the formation of mesostructures, such as the flow coating methods developed during the course of this project.

Technology Transfer

Crosby and Emrick initiated a collaboration with scientists at Saint-Gobain High Performance Materials research center focused on using inorganic nanoparticle-based mesostructures as fillers in high temperature materials.